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(54) Title : " PROCESS FOR PRODUCING A SLOW-RELEASING COPPER FERTILIZER."

(57) Abstract :

This invention relates to a process for the manufacture of slow-releasing copper fertilizer comprising of copper polyphosphate compounds. The advantage of this product over the traditional water soluble fertilizers is reduction in leaching losses, lower toxicity hazard and better nutrient use efficiency. According to the process of the present invention, cupric chloride is heated with phosphoric acid to produce low molecular weight polyphosphates, which is subsequently treated with a basic compound to convert it to the desired form. The product, which is either copper calcium polyphosphate or copper ammonium polyphosphate, can be readily used as a copper fertilizer.

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THE PATENTS ACT, 1970

COMPLETE

Specification

SECTION 10

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

having reduced water solubility do not suffer any of these disadvantages. Moreover, a constant supply of nutrient is available to meet the requirement of the crop at all stages of its growth. Although phosphate glass frits have long been proposed as a slow-releasing fertilizer, they have not attained the desired degree of popularity. This is mainly due to the fact that for the production of phosphate glass frits, high temperatures ($> 800^{\circ}\text{C}$) are required for obtaining the melt which necessitates the use of platinum containers or similar expensive materials that can resist the extremely corrosive nature of phosphoric acid at temperatures above 400°C . The present invention eliminates this difficulty by producing a non-glassy copper polyphosphate powder at much lower temperatures so that the corrosive action of phosphoric acid is greatly reduced and inexpensive materials such as ceramic-ware can be used as containers. The energy input required is also much lower.

The present invention provides a process for the manufacture of slow-releasing copper fertilizer, which process comprises (a) heating cupric chloride with water and phosphoric acid, in the proportion $100 \text{ g CuCl}_2 \cdot 2\text{H}_2\text{O} : 125 \text{ g P}_2\text{O}_5$, at 150°C , (b) adding water and further heating at 150°C , (c) repeating the process, described in stage (b) till a light greenish-blue solid with virtually no chloride ion, is formed, (d) further heating the product of stage (c) at $250^{\circ} - 350^{\circ}\text{C}$, (e) mixing the resultant mass with water, (f) treating with a basic compound such as herein described to raise the pH to 3.7 and (g) finally drying to obtain a dried powder as the desired fertilizer.

This invention relates to a process for the manufacture of slow-releasing copper fertilizer comprising of copper polyphosphate compounds. According to the process of the present invention, cupric chloride is heated with phosphoric acid to produce low molecular weight polyphosphates which is subsequently treated with basic compounds to convert it to the desired form. The product, which is either copper calcium polyphosphate or copper ammonium polyphosphate, can be readily used as a copper fertilizer.

Compounds which are popularly used as copper fertilizers are mostly soluble cupric salts or organic chelated forms such as cupric sulphate, copper-EDTA complex etc.; liquid forms such as a solution of cupric ion in condensed phosphoric acid or ammonium polyphosphates are also used (V. Sauchelli, 1969, Trace elements in Agriculture, Van Nastrand, New York; G.H. Collins, 1955, Commercial fertilizers, Reinhold, New York). There does not appear to be any existing Indian patent on slow releasing copper fertilizers of the type described here, which is essentially based on copper polyphosphate compounds.

The major drawbacks, of using soluble salts as micronutrient fertilizers, are rapid leaching losses, ground water contamination and the possibility of toxicity, since dosage requirements are usually very low. On the other hand, micronutrient fertilizers

Accordingly, this invention provides a process for producing copper polyphosphate compounds which have low water solubility, are non-toxic, non-hygroscopic and containing copper in a completely available form. The main novel feature of this invention is the use of phosphoric acid at fairly low temperatures, to produce low molecular weight copper polyphosphates. Another novel feature is the simple method for removing virtually all the chloride ions and thereby obtaining an almost pure copper phosphate salt prior to polymerisation. The presence of chloride ions interferes with the polymerisation reaction and is also deleterious to the properties of the product. A third novel feature is the elimination of hygroscopicity and reduction of water solubility of the copper polyphosphate by treatment with a basic compound such as lime, calcium carbonate or ammonia. The synthesis of short-chain polyphosphates rather than long-chain polyphosphates, ensures that the copper remains in a readily available form.

The principle underlying the production of slow-releasing copper fertilizer, according to the process of the present invention, is that when cupric chloride is heated with orthophosphoric acid in the presence of water at 150°C, hydrochloric acid is evolved with the formation of cupric phosphate. However, if the reaction mixture dries up before all the chloride ions are removed as hydrochloric acid, then a mixed cupric chloride-phosphate salt is produced from which chloride cannot be eliminated even after reaction at 300°C. Therefore, the reaction mixture must be repeatedly heated with small amounts of water which facilitates the

removal of chloride as hydrochloric acid. When chloride ions are present in the system, the mixture is dark green in colour; the colour becomes lighter as the chloride ions are removed and ultimately a very light blue coloured solid is obtained when all chloride ions are eliminated and pure cupric phosphate is obtained as the residue. Subsequently, on further heating this residue at higher temperatures, polymerisation occurs with the formation of linear polyphosphate chains. The cupric as well as hydrogen ions are bound to the oxygen atoms along the chain. When the chain length is small, the number of ions is proportionately higher and consequently the compound is soluble. As polymerisation increases, more H^+ ions are lost by dehydration and thereby the compound becomes more insoluble. In very long chain copper polyphosphates the Cu^{2+} is not readily available to plants. In smaller chain compounds, the Cu^{2+} may be solubilised by complexing agents and is, therefore, readily assimilable by plants. However, any polyphosphate always contains chains of various sizes; therefore, a part of it remains water soluble whereas another part which consists of the longer chain fraction may be highly insoluble. Both these properties are undesirable. In order to overcome this problem, a polyphosphate having a small average chain length was synthesised which did not contain any non-available Cu^{2+} forms. This was then reacted with CaO , $CaCO_3$ or NH_4OH so that the excess H^+ ions in the water soluble fraction is neutralised. This treatment causes the water soluble molecules to become almost insoluble. It also results in decrease in hygroscopicity of the sample which is, therefore, convertible to a dry powder.

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Cupric chloride, water and phosphoric acid are allowed to react at 150°C till a dry residue is obtained. This is again made into a slurry with water and the process repeated till a light blue residue is obtained. Subsequently the residue is heated at 250°C till a copper polyphosphate of the desired degree of polymerisation is produced. The polyphosphate is then mixed with water and ammonia, calcium carbonate or calcium oxide till the pH of the suspension attains a value of around 4. Finally the product is dried and ground to a powdery form. The various stages in the production of the slow-releasing copper fertilizer are described in detail below.

Cupric chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ containing up to 36.5% Cu may be used as the starting material. Every 100 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is treated with 606 ml of water and phosphoric acid containing 125 g P_2O_5 . Almost any grade and dilution of the acid (30% to 60% P_2O_5) can be used for the reaction. The mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, H_2O and H_3PO_4 taken in a porcelain crucible, is heated in a furnace at 150°C till a excess water is removed and a dry residue is obtained. Excessive drying must be avoided at this stage to prevent polymerisation of the phosphate. Again sufficient water (100 ml) is added and mixed to form a slurry and this is heated as before, at 150°C. The entire process of adding water and drying, is continued till a light green (blue) residue is obtained indicating almost complete removal of Cl^- . This residue which consists chiefly of copper phosphates, is heated at 250°C for 16 min. Polymerisation of the $\text{Cu}(\text{H}_2\text{PO}_4)_2$ occurs and the resulting polyphosphate

has an average chain length (\bar{n}) of 2.77. The total weight lost by the mixture after polymerisation is 4.6% of the total weight of H_3PO_4 . Heating at higher temperatures above $350^{\circ}C$ causes very rapid polymerisation. Controlling the degree of polymerisation at the desired level, therefore, becomes very difficult. At temperatures below $200^{\circ}C$ polymerisation is very slow. Therefore $250^{\circ}C$ is the optimum temperature for the synthesis of the copper polyphosphate although any temperature with $250^{\circ}C$ to $350^{\circ}C$ may be employed, if necessary. The reaction product is then cooled to room temperature and 300 ml water is added and mixed well to form a slurry. To this 90 g CaO or 160 g $CaCO_3$ or 204 g NH_4OH solution containing 55 g NH_3 is added and the slurry mixed well and allowed to stand for 8 - 10 hrs to ensure complete reaction. The final pH of the slurry should be around 3.7. Increasing the pH above 4.0 by addition of excess bases may cause precipitation of cupric hydroxide. On the contrary, addition of too little of the basic compound causes incomplete neutralisation of the free acid. This results in higher water solubility and hygroscopicity, both of which are undesirable characteristics. After neutralisation, the slurry is dried and ground to a powder.

The characteristics of this fertilizer are as follows : The sample which has been neutralised with NH_4OH is a copper ammonium polyphosphate and has the composition 13.8% Cu, 15.8% N and 20.7% P. That which has been neutralised with a calcium compound is a copper calcium polyphosphate of composition 12.0% Cu, 20.4% Ca and 18.1% P. The soluble Cu in these compounds are 4.6% and 3.4% for

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the ammonium and calcium forms respectively. Both these samples are 100% soluble in 0.1 N HCl, 1 N citric acid, 1 N ammonium citrate at pH 8.5, 0.02 M EDTA at pH 4.05 and 0.005 M DTPA solutions. As all these aforementioned reagents are used for assessing the availability of Cu, the tests indicate that the Cu in these fertilizers is completely available to plants. Plant growth experiments also confirm the fact that these fertilizers are efficient sources of Cu for plants and are either comparable to or better than CuSO_4 in their fertilizing action.

Example I

Cupric chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (100 g) was taken in a porcelain dish and 606 ml of water was added followed by 113 ml of phosphoric acid containing 60% P_2O_5 . The weight of the mixture was recorded. From this, the calculated weight of $\text{CuCl}_2 + \text{H}_3\text{PO}_4$ (excluding the weight of water and the weight of the crucible) was 255.7 g. It was then heated in an electric furnace at 150°C for 90 min. The residue which was almost dry, was taken out and 100 ml of water was added and mixed well. The slurry was heated once again for 60 min at 150°C . This process was repeated three times when a distinct colour change from the original dark green to a light greenish blue occurred. When a sample of this residue was dissolved in 1 N HNO_3 and tested for Cl^- with 0.1 N AgNO_3 solution only a very faint white precipitate was observed. The furnace temperature was then raised to 250°C and sample heated for 16 min. The weight of the sample after heating was 212.8 g. If after heating, the weight of the sample was observed to be

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higher, then heating was continued till the weight loss corresponded to 16.77% of the total weight of $\text{CuCl}_2 + \text{H}_3\text{PO}_4$. Once the period of heating was calibrated for a particular furnace and for a particular type of container and amount of sample, then all subsequent samples could be heated for the same period; recording the initial and final weights was, then, not necessary.

The polyphosphate sample was then mixed with 300 ml water to form a thin paste. Subsequently 160 g CaCO_3 was added to it and the mass was mixed thoroughly. After about 8 - 10 hrs the product was dried and powdered to pass through 100 mesh B.S. sieve. The material thus obtained has the composition 12.0% Cu, 20.4% Ca and 18.1% P.

Example II

The entire process was the same as in example I except that during neutralisation 90 g CaO was used instead of CaCO_3 . The composition of this sample was the same as that in example I.

Example III

The entire process was the same as in example I except that during neutralisation ammonia solution was used instead of CaCO_3 . To the slurry described in example I 227 ml ammonia solution containing 27% NH_3 was added, mixed thoroughly and the end product obtained as described in example I. The composition of this sample was 13.8% Cu, 15.8% N and 20.7% P.

We claim :

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1. A process for the manufacture of slow-releasing copper fertilizer, which process comprises (a) heating cupric chloride with water and phosphoric acid, in the proportion 100 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: 125 g P_2O_5 , at 150°C , (b) adding water and further heating at 150°C , (c) repeating the process, described in stage (b) till a light greenish-blue solid with virtually no chloride ion, is formed, (d) further heating the product of stage (c) at $250^\circ - 350^\circ\text{C}$, (e) mixing the resultant mass with water, (f) treating with a basic compound such as herein described to raise the pH to 3.7 and (g) finally drying to obtain a dried powder as the desired fertilizer.
2. A process as claimed in Claim 1 wherein the phosphoric acid used has any concentration between 30% and 60% by weight P_2O_5 .
3. A process as claimed in any of the preceding claims wherein at stage (b) water is again added to the reacted mass from stage (a).
4. A process as claimed in any of the preceding claims wherein at stage (b) the reaction is carried out at 150°C till a dry residue is obtained.
5. A process as claimed in any of the preceding claims wherein at stage (d) the reaction is carried out at 250°C for 16 min.

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6. A process as claimed in any of the preceding claims wherein the reaction in stage (d) is continued at 250°C until the weight loss due to dehydration corresponds to 16.77% of the original weight of $\text{CuCl}_2 + \text{H}_3\text{PO}_4$.
7. A process as claimed in any of the preceding claims wherein at stage (e) the reacted mass from stage (d) is treated with water and ground to a paste.
8. A process as claimed in any of the preceding claims wherein at stage (e), the amount of water used is 300 ml per 100 g CuCl_2 .
9. A process as claimed in claim 1 wherein at stage (f) 90 g CaO is used for every 100 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the mixture.
10. A process as claimed in claim 1 wherein at stage (f) 160 g CaCO_3 is used for every 100 g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the mixture.
11. A process as claimed in claim 1 wherein at stage (f) the basic compound used is a solution of ammonia.
12. A process as claimed in claim 11 wherein 55 g NH_3 is used for every 100 g CuCl_2 in the mixture.
13. A process as claimed in any of the claims 9-12 wherein at stage (f) the quantity of the basic compound that is added is sufficient to raise the pH of the mixture to 3.7.

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14. A process as claimed in any of the preceding claims wherein at stage (f) the reaction mass, after neutralisation is allowed to stand for 8 - 10 hours prior to drying.
15. A process as claimed in any of the preceding claims wherein at stage (g) the sample is powdered to pass through a 100 mesh B.S. sieve.
16. A process for the manufacture of slow-releasing copper fertilizer substantially as herein described and as illustrated in the Example(s).

✓ Sanjay Kumar Ray
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28 November 1991

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